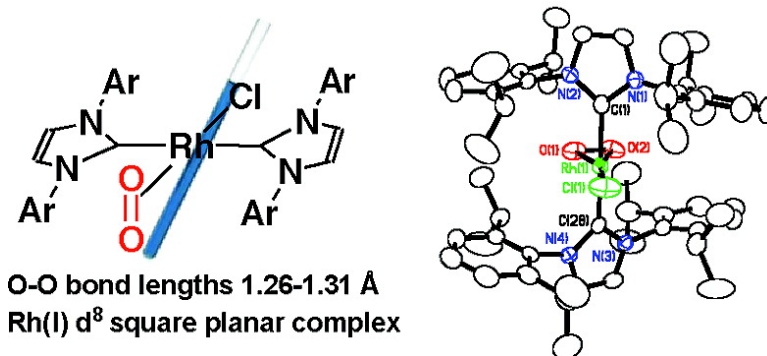


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## N-Heterocyclic Carbene Complexes of Rh: Reaction with Dioxygen without Oxidation

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The ability of transition-metal complexes to activate small molecules such as CO, N<sub>2</sub>, and O<sub>2</sub> is of significant importance in chemistry and biochemistry.<sup>1a</sup> Of these, O<sub>2</sub> activation has possibly the most significant biological implications, from reversible binding/transport of oxygen to oxidation catalysis.<sup>1b</sup> Catalytic methods for oxidation are of critical importance since such methods obviate the need to use stoichiometric oxidants such as chromium and manganese oxides. Thus, the study of metal complexes of dioxygen has been of significant interest since the pioneering work of Vaska,<sup>2a,b</sup> Ibers,<sup>2c</sup> Basolo,<sup>2d</sup> and others.<sup>2e</sup> In the realm of oxidation catalysts, Pd(II) peroxo complexes<sup>2f-i</sup> may play a key role in catalysis.

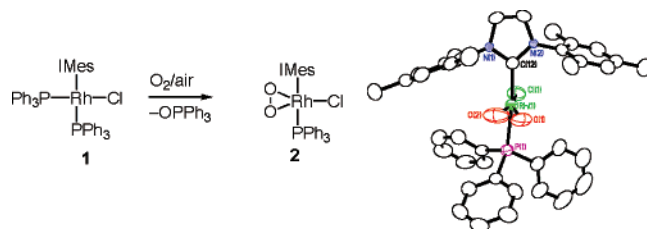
One of the challenges of developing well-defined molecular catalysts for oxidation reactions is the need to employ oxidatively stable ligands. Thus, N- and C-based ligands such as bipyridine, sparteine, and N-heterocyclic carbenes (NHC) have been successfully employed with Pd-catalyzed oxidations.<sup>3</sup> We report herein our studies of the interactions of Rh–NHC complexes with dioxygen, which remarkably occur *without oxidation* of the metal.

As part of our interest in the reactions of NHC-modified Rh complexes with small molecules such as H<sub>2</sub> and CO,<sup>3</sup> we found that the reaction of ClRh(IMes)(PPh<sub>3</sub>)<sub>2</sub> (**1**)<sup>3c</sup> with oxygen or air results in a change of color of the solution from yellow to green. From this solution, dioxygen complex (**2**) was isolated, Figure 1.

Despite considerable literature on the chemistry of Rh and Ir dioxygen complexes,<sup>2e,4</sup> compound **2** is a rare example of a formally square planar complex of molecular oxygen.<sup>4e-h</sup> In addition, the O–O bond length in **2** is unusually short (1.26 Å) compared with typical peroxo species (1.4–1.5 Å).<sup>4,5</sup> The closely related complexes [ClRh(NHC)(PN)] **3a,b**, where PN = chelated *o*-(diphenylphosphino)-*N,N*-dimethylaniline and NHC is either IPr (**3a**, IPr = *N,N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) or IMes<sup>3c</sup> (**3b**), feature O–O bond lengths of 1.450 Å.<sup>6</sup>

Further oxidation of the remaining phosphine ligand upon exposure to air or oxygen made complex **2** difficult to handle. Additionally, the crystal was composed of three independent complexes with slight variants in O–O bond lengths (Table 1). Thus, we set out to prepare non-phosphine-containing analogs of **2**. Treatment of [Rh(H<sub>2</sub>C=CH<sub>2</sub>)<sub>2</sub>Cl]<sub>2</sub> with 2 equiv of IPr or IMe under N<sub>2</sub> gave yellow solutions which were then exposed to air or oxygen. After several hours, the reactions began to darken, giving deep blue solutions from which X-ray quality crystals were obtained.

Complexes **4** (IPr) and **5** (IMes) were also square planar, exhibiting unusually short O–O bond lengths as low as 1.267(13)

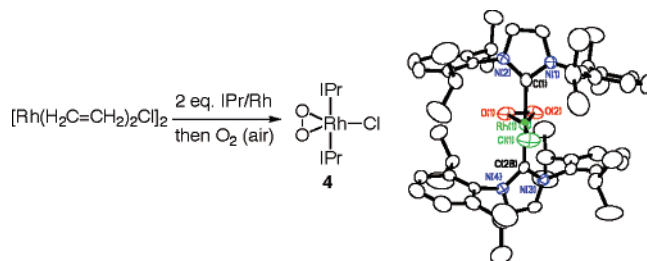


**Figure 1.** Preparation of compound **2** from **1**. Thermal ellipsoids are drawn at 50%, and hydrogen atoms are omitted for clarity.

**Table 1.** O–O Bond Lengths in Selected M–O<sub>2</sub> Complexes

entry	complex	O–O (Å)
1	ClRh(IMes)(PPh <sub>3</sub> )(O <sub>2</sub> ), <b>2</b>	1.26 <sup>a</sup>
2	ClRh(IPr) <sub>2</sub> (O <sub>2</sub> ), <b>4</b>	1.315(3)
3	ClRh(IMes) <sub>2</sub> (O <sub>2</sub> ), <b>5</b>	1.267(13), 1.271(14)
4	ClRh(NHC)(PN)(O <sub>2</sub> ), <b>3a, 3b</b> <sup>b</sup>	1.450(2), 1.450(3)

<sup>a</sup> Average of three components of the crystal at 1.249(9), 1.298(9), and 1.231(16) Å. Note O<sub>2</sub> itself is 1.21 Å. <sup>b</sup> **3a**, NHC = IPr; **3b**, NHC = IMes.



**Figure 2.** Synthesis and X-ray crystallographic structure (ORTEP drawing) of ClRh(IPr)<sub>2</sub>(O<sub>2</sub>). Thermal ellipsoids are drawn at 50%, and hydrogen atoms are omitted for clarity.

Å (see Table 1), and are diamagnetic. The ORTEP drawing of **4** is given in Figure 2, and details of the structure determination of **5** are found in the Supporting Information. Although complex **5** is comprised of two different forms in the crystal structure, resulting from disorder of the Cl and O<sub>2</sub> ligands, **4** contains no such disorder and still sports an unusually short O–O bond.

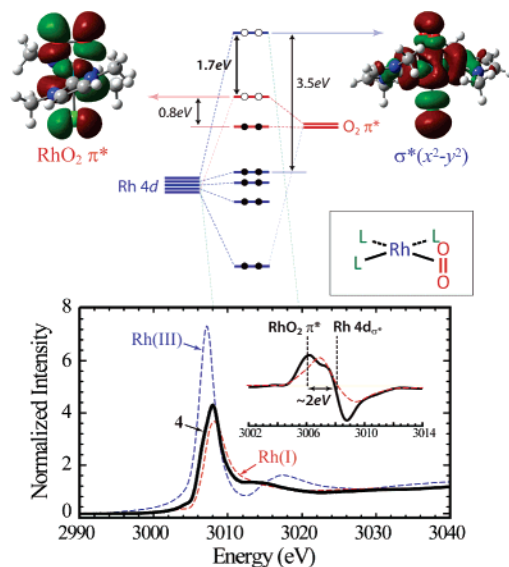
Considering the difficulties that can be associated with the accurate determination of O–O bond lengths,<sup>7</sup> we analyzed the IR and Raman spectra of complex **4**. Given the unusually short O–O bond distances, one would expect larger  $\nu_{O-O}$  than observed in typical peroxo complexes (750–900 cm<sup>-1</sup>). Although the IR spectrum of **4** is complex, Raman excitation at 568 nm (into a low-energy absorption of the complex) provides resonance enhancement of a band at 1010 cm<sup>-1</sup>. Based on the loss of this band and the emergence of another at ~960 cm<sup>-1</sup> in the <sup>18</sup>O<sub>2</sub> isotopomer, this is assigned as the O–O stretch. These data are consistent with a

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**Figure 3.** Top: Schematic energy level diagram of DFT-calculated valence MOs for **4**. Orbitals are colored based on dominant atomic contributors. Bottom: Rh  $L_3$ -edge XAS data: **4** (black),  $\text{RhCl}_3$  (blue, dashed), and  $\text{Rh}(\text{IPr})(\text{OAc})(\text{CO})_2$  (red, dashed). Inset: first derivative of data for **4** and **7**.

stronger O–O bond such as would generally be observed in  $\text{O}_2^-$  (superoxide) species, suggesting a possible  $\text{Rh}(\text{II})-(\text{O}_2^-)$  electronic structure for these complexes. Considering the rarity of side-on superoxo complexes in general, and the absence of such complexes for Rh in particular, we examined the electronic structure of the complexes by Rh L-edge X-ray Absorption Spectroscopy (XAS) to evaluate the 4d orbital occupancy in **4** from the intensity of the dipole-allowed  $\text{Rh } 4d \leftarrow 2p$  transitions (Figure 3).

Figure 3 shows the Rh  $L_3$ -edges for **4**, which clearly indicate a valence d orbital occupation consistent with a  $\text{Rh } 4d^8$  species. Thus, a single empty valence orbital [ $\text{Rh } 4d_{\sigma^*}(x^2-y^2)$ ] and thus a single main feature in the spectrum is expected.<sup>8</sup> The observation of a shoulder  $\sim 2$  eV below the main feature at 3009 eV can be understood after consideration of DFT calculations performed on the *N*-Me derivative of **4**. The resultant valence MO diagram (Figure 3, top) is consistent with a square planar  $\text{Rh } 4d^8$  metal center coordinated by *singlet* dioxygen, which is consistent with all available data. It also provides a rationale for the low-energy shoulder in the XAS data:  $\pi$ -backbonding from Rh into an empty  $\pi^*$  orbital of the dioxygen ligand ( $\text{RhO}_2 \pi^*$ ) stabilizes the singlet ground state and provides for intensity into the  $\text{RhO}_2 \pi^* \leftarrow \text{Rh } 2p_{(3/2)}$  transition (Figure 3, bottom inset).<sup>9</sup> Furthermore, this electronic description explains the superoxide-like O–O stretching frequency given that the two major  $\text{Rh}-\text{O}_2$  bonding interactions both serve to decrease the bond stretching frequency but essentially cancel each other with respect to charge delocalization.

Thus it appears that the best description of the bonding is  $(\text{Rh } 4d^8) - (\text{O}_2)$ , i.e., square planar  $\text{Rh}(\text{I})$  bound to singlet oxygen.<sup>10</sup> This motif represents a fundamentally different mode of binding for dioxygen, which has already yielded a surprisingly broad range of binding modes with transition metals.<sup>1,2</sup>

Based on this work and existing literature, it is likely that previous examples of Rh “peroxo” species with unusually short O–O bond lengths also correspond to this novel bonding motif, which together form a previously unrecognized class of transition-metal–singlet dioxygen adducts. Interestingly, it appears that strong field ligands may favor formation of singlet  $\text{O}_2$  adducts. For example,  $\text{ClRh}(\text{PR}_3)_2$  form four-coordinate dioxygen adducts with O–O stretches of 993 and 990  $\text{cm}^{-1}$  when  $\text{R} = \text{Pr}$  or  $\text{Cy}$ ,

respectively.<sup>4e,f</sup> However, the corresponding  $\text{PPh}_3-\text{O}_2$  complex is five-coordinate with an O–O distance of 1.413(9) Å.<sup>4a</sup> Milstein’s square planar  $\text{O}_2$  complex bearing an electron-rich PCP-pincer ligand<sup>4g</sup> also features a short O–O bond. Although no vibrational or XAS data were reported, the observation of a large  $^1J_{\text{Rh}-\text{P}}$  led the authors to speculate that this complex may be best described as an adduct between  $\text{Rh}(\text{I})$  and dioxygen.<sup>4g</sup> Since a new type of reactivity may be associated with this mode of bonding, obtaining a clear picture of the  $\text{Rh}-\text{O}_2$  interaction is critical.

In conclusion, we have synthesized  $\text{NHC}-\text{Rh}$  complexes which bind dioxygen giving square planar complexes with no net change in the oxidation state of the metal. The effect that this unique bonding arrangement has on reactivity is under assessment.

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**Supporting Information Available:** Spectral data, X-ray structure determinations, tables of  $\text{Rh}-\text{O}_2$  complexes and side-on superoxo complexes, molecular orbital calculations, and their results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The spectra for such complexes are only marginally affected by multiplet effects in the low-energy part of the spectrum due to the very large LF splitting as observed by the 3.5 eV splitting in Figure 3. A simple MO analysis of the excited-state structure is thus qualitatively appropriate.
- This  $\pi$ -backbonding interaction involves the  $\text{O}_2 \pi^*$  orbital similar to that in the  $\text{Cu}(\text{II})$ -superoxo systems of Solomon et al., but the magnitude of the interaction is smaller in the Rh complexes, and the empty orbital is thus ligand-based, implying a  $4d^8$  configuration.
- Rh and Ir– $\text{O}_2$  complexes prepared using generated singlet oxygen,<sup>4b</sup> however, have bond lengths and geometries typical of  $\text{Rh}(\text{III})$  complexes.

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